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<p>(21) International Application Number: PCT/US97/06713 (22) International Filing Date: 23 April 1997 (23.04.97) (71) Applicant (for all designated States except US): ELMER'S PRODUCTS, INC. [US/US]; 180 E. Broad Street, Columbus, OH 43215 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): COLUMBUS, Peter, Spiros [US/US]; 31 Hilltop Drive, Melville, NY 11747 (US). ANDERSON, John [US/US]; 4164 Checkerberry Court, Hilliard, OH 43026 (US). (74) Agent: PAVELKO, Thomas, P.; Watson Cole Stevens Davis, P.L.L.C., Suite 1000, 1400 K Street, N.W., Washington, DC 20005-2477 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i></p>
<p>(54) Title: ADHESIVE APPLICATOR CRAYON (57) Abstract Adhesive compositions exhibiting fast cure time in solid form, e.g. in the form of an applicator crayon or glue stick. The adhesive exhibiting polymer of the composition is based on a mixture of critical amounts of high molecular weight polyvinylpyrrolidone polymer, with a lower molecular weight polyvinylpyrrolidone polymer, with water, an organic solvent, and a salt of a long-chain fatty acid, e.g. sodium stearate. Color indicators and other optional ingredients, e.g. mildewcide, can be included.</p>		

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ADHESIVE APPLICATOR CRAYON

Background of the Invention

1. Field of the Invention

Fast setting adhesive formulations in an easy applicator form are desirable for office, school and home consumers. The present invention provides a polyvinylpyrrolidone (hereinafter "PVP")-based composition in solid form, e.g. glue stick or crayon, which is easy to apply, bonds faster and is safe to use. The adhesive bonds porous substrates to which they are applied, such as paper, fabrics, polystyrene foam, wood and similar porous substrate materials.

2. Description of the Related Art

U.S. Patent 3,576,776, issued in 1971, contains a disclosure of an invention for adhesive applicator crayons comprising a shape-giving base consisting of a gel-forming salt, a liquid, and an adhesive component. Among the adhesives are listed salts of various acids, amides, and N-alkyl substituted amides including polyvinylpyrrolidone. The disclosure of U.S. patent 3,576,776 was said to be an improvement over known adhesive applicator crayons prepared from rubber, resins and waxes, which required that surface layers must be rubbed off from such crayons under relatively high pressure in order to carry out the spreading of the adhesive.

Later solid adhesive compositions, such as those disclosed in U.S. Patents 4,073,756 and 4,075,830, were said to avoid the problem inherent in the crayons of U.S. Patent 3,576,776, the long time it took to produce the adhesive composition and the high viscosity of the adhesive composition (e.g.

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higher than 150,000 cps) which made it difficult to fill the adhesive composition in containers.

The later patents thus used water soluble or water dispersible polymers having adhesive properties in combination with N-fatty acid acylated amino acids or salts thereof and water, or a mixture of water and one or more organic solvent(s) and/or plasticizer(s). The water dispersible or water soluble polymers having adhesive properties listed, among others, homopolymers or copolymers having a carboxyl group or a carboxylic anhydride group, where the proportions of the carboxyl and/or carboxylic anhydride group containing monomer is preferably about 30 to 100 mol %.

These, and other prior art formulations (the entire disclosures of all of which are herein incorporated by reference), were still slow to exhibit adhesive properties when dispensed, i.e. slow to exhibit paper tear when applied to bond paper.

Among other properties, the present invention provides strong final bonds and a pH generally in the range of about 8.5 to about 9.5. However, in the embodiments of the invention where a color indicator is used, the hue or intensity of the color is enhanced by having a pH more alkaline than the range given above, e.g. up to a pH of about 11, e.g. 10.9 - 11.1.

Object of the Invention

It is thus an object of the invention to provide new adhesive compositions exhibiting fast adhesive properties (e.g. fast initial tear of paper) and strong final bonds.

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It is a further object of the invention to provide adhesive compositions in the form of solids at ambient conditions, i.e. glue sticks or applicator crayons which exhibit fast adhesive properties when applied to a substrate and suitable for bonding paper, fabric, polystyrene foam and similar materials.

It is a still further object of the invention to provide bonded substrates, such as paper, fabric, and similar porous materials, bonded with the adhesive compositions of the invention.

Summary of the Invention

Water-based solid adhesive crayons which contain water in a mixture comprising a relatively low molecular weight (all references to "molecular weight" in this Specification, claims and Abstract are intended to mean "weight average molecular weight" unless otherwise designated) water dispersible or water soluble polymer, e.g. polyvinylpyrrolidone polymer, i.e. a molecular weight below about 1,300,000, and a critical amount of a relatively high molecular weight water dispersible or water soluble polymer, e.g. polyvinylpyrrolidone polymer, i.e. a molecular weight above 1,300,000. By critical amounts is meant sufficient amounts of the high molecular weight (polyvinylpyrrolidone) polymer to impart 1.) a fast film-forming or setting property, 2.) a strong final bonding property, and 3.) an additional firmness to the crayon adhesive to reduce "crumbling" when pressure is applied to the crayon, while keeping the water content of the adhesive at 50 weight percent, or more, to ensure easy spreading and performance during use and after storage. Optional ingredients include a plasticizer for the (polyvinylpyrrolidone) polymers to impart a degree of flexibility to the dry

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adhesive film, a preservative to protect the adhesive from attack by microorganisms, a long chain fatty acid salt to impart a solid gel property to the adhesive, and a color indicator for the purpose of indicating when an applied film of adhesive has dried.

This composition may be formulated so as to exhibit physical properties of a solid, e.g. it may be formulated so as to be suitable for application in the form of a crayon or glue stick to porous substrates to be bonded. The composition is preferably formulated so as to be satisfactorily extruded from and retracted into a container, exhibit good spreadability without being "runny" or dispensing excessive adhesive to a substrate nor so firm that the crayon or adhesive stick "crumbles" due to the requirement to exert excessive pressure during application of the crayon/stick to a substrate to effect adequate spreading of the adhesive on the substrate.

It is also within the purview of the invention to provide substrates bonded with the formulations of the invention.

Detailed Description of the Invention

The composition of matter of this invention exhibits adhesive properties and is formulated of components (A), (B), (C), and (D), wherein (A) is an aqueous vehicle, typically water or aqueous emulsions/dispersions of one or more of components (B), (C), (D) and/or any optional components; (B) is at least one water soluble or water dispersible polymer, e.g. polyvinylpyrrolidone (hereinafter "PVP") polymer exhibiting adhesive properties having a molecular weight below about 1,300,000, (C) is a salt of a long chain fatty acid or a precursor thereof which forms a salt of a long chain

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fatty acid when combined with the other components of the compositions of matter of this invention and (D) is a water soluble or water dispersible polymer, e.g. a PVP polymer having a molecular weight above about 1,300,000, preferably above about 2,000,000 most preferably of at least about 2,800,000. Suitable polymers for component (B) include homopolymers or copolymers of the types identified in U.S. Patents 4,073,756 or 4,954,544, although PVP is particularly preferred. Although higher molecular weight polymers of component (D) can be of the same type of polymer as component (B), it is preferred that the high molecular weight polymer be PVP.

When it is desirable, certain optional ingredients may be included in the composition of matter of the invention, e.g. a mildewcide and/or fungicide, solvents for the adhesive exhibiting polymeric components, e.g. alcohols, such as glycerol or polyglycols for PVP, pigments and/or dyes to impart a permanent color, and/or a color indicator, such as phenolphthalein or thymolphthalein, for indicating when the applied film is dried.

Generally, the components of the invention may be combined over a wide range. However, in order to formulate the composition of matter in solid form, e.g. suitable for use, as an adhesive applicator stick or crayon, it is preferable that the composition contain not less than about 50% nor more than about 80% (all % in this application are by weight unless otherwise noted) by weight of component (A) (wherein (A) is water). If (A) is an aqueous formulation containing one or more components (B)-(D), or having optional components, the amount of (A) can be adjusted so as to be greater than, or lesser than, the amounts indicated. Although it is preferable that the

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composition contain not less than about 50%, preferably not less than about 60% of component (A) (where (A) is water) this amount can be adjusted lower, e.g. 45% or less though not exhibiting the most preferred properties of the adhesive stick of the invention. The presence of plasticizers, solvents or mixtures thereof for the water dispersible polymers may also decrease the requirements for component (A) to be present in an amount of not less than 50%, because such plasticizers/solvents enhance the spreadability properties. As with the case of the maximum content of component (A), when (A) is an aqueous formulation containing one or more of components (B)-(D), or any optional components, the amount of (A) will be adjusted accordingly.

Component (B) is at least one polymer exhibiting adhesive properties, preferably a polyvinylpyrrolidone (PVP) of relatively low molecular weight, e.g. below about 1,300,000. PVP polymers are commercially available in several viscosity grades, ranging from very low to very high molecular weight. This range, coupled with solubility in water, aqueous and organic solvent systems and its non-toxic character, give PVP great flexibility in the compositions and applicator solid forms of the present invention.

Commercially available PVP suitable for use in this invention as components (B) or (D) are available from GAF Chemicals Corporation, International Specialty Products, of Wayne, N.J., U.S.A., under the tradenames PVP K-90 and PVP K-120, each having an off-white powder appearance. PVP K-90 has a viscosity average molecular weight of 630,000 (performed at 25°C, in H₂O, using Mark Houwink constants of $K = 1.4 \times 10^{-4}$ and $a = 0.7$), a weight average molecular weight (Wt.Avg.MW) of 1,280,000 (obtained by

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low angle laser light scattering (LALLS) photometry) and a K-value of 88-100. PVP K-120 has a viscosity average molecular weight of 1,450,000 (performed under the same conditions above); a weight average molecular weight of 2,800,000 (performed by LALLS photometry as above) and a K-value of 115-125. These same polymers are also available as solutions from the same source. Other commercially available PVP in powder or solution form can be obtained from BASF Corporation of Mount Olive, N.J., U.S.A. under the registered trademark LUVISKOL over a wide range of molecular weights. Luviskol K-90 has a weight average molecular weight of 1,200,000; Luviskol K-80 has a weight average molecular weight of 900,000 and Luviskol K-60, K-30 and K-77 have lower molecular weights. These products are described in the Luviskol® Polyvinylpyrrolidone Polymers catalog by BASF corporation and PVP Polyvinylpyrrolidone Polymers catalog by ISP (International Specialty Products) GAF corporation, the entire disclosures of which are herein incorporated by reference.

It is to be expressly understood that the identification of the aforementioned commercially available sources of PVP polymers and/or solutions is by way of illustration only and not by way of limitation; as other commonly available sources or synthesized polymers may be used in the invention without departing from the spirit or scope of the appended claims.

Preferably, in the compositions of the invention, component (B) is present in amounts of at least about 12% but not more than about 26%. More than one low molecular weight polymer can be used as component (B). When more than one low molecular weight adhesive-exhibiting polymer is present,

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it is preferable that the higher molecular weight polymer of such low molecular weight polymers is present in an equal or greater amount.

Component (C) is generally present from about 3% to about 10%, based on the total weight of the composition, preferably in the range of about 6% to about 8%. Component (C) is a long chain (i.e. C_{15} - C_{26}) fatty acid, preferably in the form of a salt with an alkali-metal or alkaline earth metal, e.g. Li, Na, K, Ca, Sr, Ba, most preferably sodium stearate. It enhances spreading properties when the crayon or glue stick is rubbed against a porous substrate.

Component (D) is a high molecular weight (e.g. above about a molecular weight of 1,300,000, preferably above 2,000,000, most preferably at least 2,800,000) polymer, e.g. PVP. The amount of component (D) is sufficient to impart fast setting properties, e.g. preferably in less than 20 seconds, preferably less than 15 seconds to the film applied to a porous substrate from the glue stick of the invention. However, the amount of component (D) should not be so great as to induce crumbling when pressure is applied to the glue stick upon rubbing the stick on the porous substrate. The amount of component (D) will vary with the molecular weight of the polymer, lower amounts being required with the highest molecular weights. In general, component (D) may be present in an amount of from about 0.5% to about 10%, preferably about 0.5% to about 4%. Most preferably, the amount of component (D) is at least 0.5 wt %, preferably at least 0.7 wt %, most preferably at least about 1 wt %.

When a solvent for the water dispersible polymer, e.g. PVP, is present, it is preferably an organic solvent. Preferably the solvent is an alcohol; more

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preferably an alcohol selected from the group consisting of glycerol, polyglycols, especially low molecular weight polyglycols, e.g. propylene glycol and mixtures thereof, though most preferably, glycerols and propylene glycol. Other solvents, including acids, ketone and ether alcohols, lactones, lactams, certain esters, ketones and chlorinated hydrocarbons; esters and nitroparaffins are known solvents for PVP. The solvent is present in amounts ranging from about 3% to about 8%, preferably about 3.2% to about 7%.

Plasticizers for the water soluble/dispersible polymers may also be included in the formulations of the inventions. Low molecular weight polyethylene glycols, e.g. having a M.W. of 400 or less, are particularly good plasticizers.

The compositions of the invention can be made by mixing components (A)-(D), and any optional components, in any order. During this mixing, temperature can be elevated to 85-95°C and mixing continued with slow agitation until components (B) and (D) are completely dissolved (within about 15 minutes) and the component (C) and any optional ingredients added and mixed until dissolved completely. Alternatively, components (A) can be mixed with (C) and/or any optional components and then mixed with the polymer components (B) and (D). Still further components (A), (B) and (D) can be mixed, or components (B) and (D) can be in solution/dispersion form, before being mixed with any other component. The resulting composition can be extruded directly into glue stick containers or drawn off into drums for storage to be reheated and used at a future date.

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When an optional component for controlling microorganisms is added, it may take the form of a mildewcide and/or fungicide. Suitable substances are commercially available, such as the mildewcide sold under the trademark "DOWICIL 150" (available from Dow Chemical Corporation, Midland, Michigan, USA) in an effective amount, e.g. as little as 0.18 wt % to 0.20 wt %.

Permanent color can be imparted to the composition of the invention by including pigments and/or dyes as an optional component.

When a color indicator is added for the purpose of indicating when the film has dried, the freshly applied adhesive has a color, e.g. blue, which fades to colorless when the adhesive has dried, e.g. in about 9-15 seconds. When the color indicator is present in combination with a permanent color, the color will change from the as applied to dried adhesive, rather than fade to colorless.

As suitable indicators can be used phenolphthalein (chemical name 3,3-bis(4-hydroxyphenyl)-1-(3H)-isobenzofuranone) or thymolphthalein (chemical name 3,3-bis[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl]-1-(3 H)-isobenzofuranone). These indicators are commercially available such as phenolphthalein and its alkyl derivatives. The indicators are present in an effective amount to indicate a change between a color and colorless phase and generally are present in an amount of not more than 2 wt % preferably from about 0.01 to about 0.5 wt %. As mentioned hereinabove, higher alkalinity enhances the intensity of these indicators to impart a stronger hue to the color exhibited.

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The advantages of the compositions of the invention will be illustrated by the following Examples and Comparative Examples. In the Examples, it can be seen that the properties of the composition, especially properties of extension and retraction of the composition from a container and most importantly its spreading and setting characteristics, can be tailored by proportioning the components.

Examples	Composition Formulation		Net Weight Stick	GEL	COLOR	Setting Time	Extension	Retraction	Spreading Properties
	Chem.	GMS.							
1	Water PVP 90 PVP 120 Glycerol Na Stearate Dowicil	60.10 24.70 01.00 07.00 07.00 <u>00.20</u> 100.00	22 g	Firm	Creamy white	12 sec.	Some resistance to extension	Failed*	Slight difficulty in spreading. Required additional pressure which applied excessive adhesive
2	Water PVP 90 PVP 120 Glycerol Na Stearate Dowicil 150	60.10 25.00 00.70 07.00 07.00 <u>00.20</u> 100.00	22 g	Firm	Creamy white	11 sec.	Slight resistance to extension	Failed*	Some difficulty in spreading, but better than Ex. 1... no crumbling
3	Water PVP 90 PVP 120 P.G. Na Stearate Dowicil 150	60.10 24.70 01.00 07.00 07.00 <u>00.20</u> 100.00	22 g	Less firm than Ex. 1 and 2	Creamy white	15 sec.	Easy	Easy	Easier spreading but excess glue applied due to softness
4	Water PVP 90 PVP 120 P.G. Glycerol Na Stearate Dowicil 150	60.10 24.70 01.00 03.50 03.50 07.00 <u>00.20</u> 100.00	22 g	Firm	Creamy white	9 sec.	Easy	Easy	Easy spreading, no crumbling

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5	Water 60.10 PVP 90 24.70 PVP 120 01.00 P.G.' 01.50 Glycerol 05.50 Na Stearate 07.00 Dowicil 150 <u>00.20</u> 100.00	22 g	Slightly soft	Creamy white	9-10 sec.	Easy	Easy	Easy spreading, no crumbling
6	Water 60.10 PVP 90 24.95 PVP 120 00.75 P.G.' 03.50 Glycerol 03.50 Na Stearate 07.00 Dowicil 150 <u>00.20</u> 100.00	15 g	Firm	Creamy white	9 sec.	Easy	Easy	Easy spreading, no crumbling
7	Water 60.10 PVP 90 25.20 PVP 120 00.50 P.G.' 03.50 Glycerol 03.50 Na Stearate 07.00 Dowicil 150 <u>00.20</u> 100.00	15 g	Slightly soft	Creamy white	9 sec.	Easy	Easy	Ever so slight spreading resistance due to slightly softer stick; no crumbling
8	Water 60.10 PVP 90 25.00 PVP 120 00.70 Glycerol 08.00 Na Stearate 06.00 Dowicide <u>00.20</u> 100.00	22 g	Slightly less firm	Creamy white	11 sec.	Easy	Failed*	Slight crumbling
9	Water 60.97 Propylene Glycol 3.33 Glycerol 3.33 PVP 90 23.76 PVP K-120 0.71 Thymol-pnthalain 0.24 Na Stearate 6.67 Sodium Hydroxide Pellets 0.20 Water (Deionized) 0.60 Dowicil 150 <u>0.19</u> 100.00	22 g	Firm	Blue when applied, colorless when dry	9 sec.	Easy	Easy	Easy spreading, no crumbling
Comparative 1	UHU Stic	21 g	Firm	White opaque	28-30 sec.	Easy	Easy	Easy spreading, no crumbling
Comparative 2	Ross Envelope	8.5 g	Firm	Creamy white	25 sec.	Easy	Easy	Easy spreading, no crumbling
Comparative 3	Ross Kidstik	8.5 g	Firm	Fuchsia/purple	23 sec.	Easy	Easy	Easy spreading, no crumbling

Compara- tive 4	Avery	7.4 g	Slightly less firm	Creamy white- white	25 sec.	Easy	Failed*	Spreads with some resistance due to a slightly less firm stick
Compara- tive 5	3M Scotch	7.08 g	Firm	Creamy white	20 sec.	Easy	Easy	Easy spreading, no crumbling
Compara- tive 6	Water 60.10 PVP 30 ¹ 25.70 P.G. ¹ 03.50 Glycerol 03.50 Na Stearate 07.00 Dowicil 150 <u>00.20</u> 100.00	22 g	Very soft	Creamy white	>than 15 min.	Easy	Easy	Spreads with some resistance due to glue crumbling
Compara- tive 7	Water 60.10 PVP 30 ¹ 12.85 PVP 90 12.85 P.G. ¹ 03.50 Glycerol 03.50 Na Stearate 07.00 Dowicil 150 <u>00.20</u> 100.00	22 g	Very soft	Creamy white	90 sec.	Easy	Easy	Spreads with some resistance due to the glue's softness; some crumbling
Compara- tive 8	Water 60.10 PVP 90 25.70 P.G. ¹ 03.50 Glycerol 03.50 Na Stearate 07.00 Dowicil 150 <u>00.20</u> 100.00	22 g	Slightly soft	Creamy white	25 sec.	Easy	Easy	Spreads with some resistance due to the glue's softness; some crumbling
Compara- tive 9	Water 75.62 PVP 120 12.00 P.G. ¹ 03.60 Glycerol 03.60 Na Stearate 07.00 Dowicil 150 <u>00.18</u> 100.00	22 g	Firm	White opaque	None after 10 min.	Easy	Easy	Very smooth spreading; however, appears that either glue is absorbed in the paper or the amount of glue transferred is minimal. Very little if any dried glue residue is felt on the paper. No low M.W. adhesive. Even when water content approaches upper limit high M.W. adhesive does not spread.

Comparative 10	Water	81.29	22 g	Soft	White opaque	4 min.	Easy	Easy	Spreads easily, doesn't crumble but loses its form and flattens when applied
	PVP 120	12.00							
	P.G. ¹	01.63							
	Glycerol	01.63							
	Na Stearate	03.25							
	Dowicil 150	00.20							
		100.00							

¹Propylene glycol

²Wt.Avg.MW = 55,000

*Glue stick separated from the carry platform.

It can readily be seen that the compositions of matter of the present invention, in the form of glue sticks or crayons, provide a fast setting, non-toxic composition suitable for adhering porous substrates.

It is to be understood that, in the specification and accompanying claims, the formulations are considered to consist of components of two phases, e.g. liquids and solids. The liquid phase component is water or aqueous phase and all other components are considered solids, even though some components used in the invention may be thought of as liquids. The percentage of solids can thus be calculated by subtracting the percentage of liquid component from 100%. For example, if the liquid phase is 70% by weight, the solid phase is 30% by weight ($100\% - 70\% = 30\%$). It thus can be appreciated that the formulations of the invention comprise a minor to equivalent percentage of solids to liquid, but yet are fast setting, strong bond forming adhesive compositions.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to those skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

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We Claim:

1. A composition of matter comprising a mixture of the following components (A)-(D):

- (A) about 45% to about 80% by weight water;
- (B) about 12% to about 26% by weight of at least one water soluble or water dispersible polymer exhibiting adhesive properties, said polymer having a molecular weight of less than about 1,300,000; ~~1,300,000~~
- (C) a long-chain fatty acid, or a salt of a long-chain fatty acid, in an amount of from about 3% to about 10%; and
- (D) a high molecular weight water soluble or water dispersible polymer, said high molecular weight polymer having a molecular weight of at least 1,300,000 and being present in an amount sufficient to impart fast film forming and strong final bonding property to the composition. ~~1,300,000~~

2. The composition of claim 1 wherein the component (B) is at least one polyvinylpyrrolidone polymer.

3. The composition of claim 1 wherein component (B) comprises at least two polyvinylpyrrolidone polymers, the polymers having different molecular weights.

4. The composition of claim 3 wherein the weight ratio of the polyvinylpyrrolidone of lower molecular weight to the polyvinylpyrrolidone of greater molecular weight is not greater than about 1:1.

5. The composition of claim 1 wherein component (D) is present in an amount of from about 0.5 to about 4% by weight.

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6. The composition of claim 1 wherein component (C) is sodium stearate.
7. The composition of claim 1 further comprising a component selected from the group consisting of glycerol, propylene glycol and mixtures thereof.
8. The composition of claim 1 further including a color indicator.
9. An adhesive crayon comprising the composition of claim 1 in solid form.
10. An adhesive crayon according to claim 9 wherein the water content is at least 50% by weight.
11. Porous substrates adhered by an adhesive formulation of claim 1.
12. The porous substrates of claim 11 wherein the porous substrate is selected from the group consisting of paper, wood, fabric and polystyrene foam.
13. A composition of matter in solid form at ambient conditions comprising:
 - (A) from about 45% to about 80% by weight of water;
 - (B) from about 12% to about 26% of at least one polyvinylpyrrolidone polymer of molecular weight less than about 1,300,000.
 - (C) from about 3% to about 10% of a long chain fatty acid or salt thereof; and

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(D) from about 0.5% to about 4% of a polyvinylpyrrolidone polymer having a molecular weight in the range of from about 1,300,000 to about 2,800,000.

14. The composition of claim 13 wherein component (A) is present in an amount of at least 50% by weight.

15. The composition of claim 13 further comprising an effective amount of a mildecide.

16. The composition of claim 13 further comprising a color indicator in an amount of from about 0.01% to 0.5% by weight.

17. Porous substrates adhered by an adhesive formulation of claim 13.

18. The porous substrates of claim 16 wherein the porous substrate is selected from the group consisting of paper, wood, fabric and polystyrene foam.

19. The composition of claim 13 further comprising at least one component selected from the group consisting of solvents, plasticizers and mixtures thereof.

20. The composition of claim 13 wherein component (C) is sodium stearate.

21. The composition of claim 13 further comprising a color indicator selected from the group consisting of phenolphthalein and thymolphthalein.

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22. An adhesive crayon comprising the composition according to claim 13 in solid form wherein the solid phase is from about 30% to about 50% by weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/06713

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08K 5/09

US CL : 524/322

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/322

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,576,776 A (MUSZIK et al.) 27 April 1971, column 4, lines 56-66.	1-22
A	US 3,787,345 A (DICKMAN et al.) 22 January 1974, column 4, lines 40-53.	1-22
A	US 4,073,756 A (YOTSUYANAGI et al.) 14 February 1978, column 4, lines 56-66.	1-22
A	US 4,075,830 A (NAGASAWA et al.) 28 February 1978, column 1, lines 45-60.	1-22
A	US 4,325,851 A (COLON et al.) 20 April 1982, column 7, lines 17-40.	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

"S"	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (to be specified)	"Z"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

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